F ENT COOPERATION TREA

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION RELATING TO PRIORITY CLAIM

(PCT Rules 26bis.1 and 26bis.2 and Administrative Instructions, Sections 402 and 409)

To:

SILVERMAN, Warren
Haseltine Lake & Co.
Imperial House
15-19 Kingsway
London WC2B 6UD
ROYAUME-UNI

Date of mailing (day/month/year) 26 July 1999 (26.07.99)	
Applicant's or agent's file reference HL58057/003/WS	**IMPORTANT NOTIFICATION**
International application No. PCT/GB99/01236	International filing date (day/month/year) 22 April 1999 (22.04.99)
Applicant MULTICORE SOLDERS LIMITED et al	

The applicant is hereby **notified** of the following in respect of the priority claim(s) made in the international application.

1. [X] **Correction of priority claim.** In accordance with the applicant's notice received on: 22 July 1999 (22.07.99), the following priority claim has been corrected to read as follows:

GB 29 September 1998 (29.09.98) 9821162.6

- [ ] even though the indication of the number of the earlier application is missing.
- [ ] even though the following indication in the priority claim is not the same as the corresponding indication appearing in the priority document:

2. [ ] **Addition of priority claim.** In accordance with the applicant's notice received on: , the following priority claim has been added:

- [ ] even though the indication of the number of the earlier application is missing.
- [ ] even though the following indication in the priority claim is not the same as the corresponding indication appearing in the priority document:

3. [ ] As a **result of the correction and/or addition** of (a) priority claim(s) under items 1 and/or 2, the (earliest) priority date is:

4. [ ] **Priority claim considered not to have been made.**

- [ ] The applicant failed to respond to the Invitation under Rule 26bis.2(a) (Form PCT/IB/316) within the prescribed time limit.
- [ ] The applicant's notice was received after the expiration of the prescribed time limit under Rule 26bis.1(a).
- [ ] The applicant's notice failed to correct the priority claim so as to comply with the requirements of Rule 4.10.

The applicant may, before the technical preparations for international publication have been completed and subject to the payment of a fee, request the International Bureau to publish, together with the international application, information concerning the priority claim. See Rule 26bis.2(c) and the PCT Applicant's Guide, Volume I, Annex B2(IB).

5. [X] In case where **multiple priorities** have been claimed, the above item(s) relate to the following priority claim(s):

GB 29 September 1998 (29.09.98) 9821162.6

6. A copy of this notification has been sent to the receiving Office and

- [X] to the International Searching Authority (where the international search report has not yet been issued).
- [X] the designated Offices (which have already been notified of the receipt of the record copy).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland**	Authorized officer R. Chrem
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREA.T

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark Office
Box PCT
Washington, D.C.20231
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 09 December 1999 (09.12.99)	
International application No. PCT/GB99/01236	**Applicant's or agent's file reference** HL58057/003/WS
International filing date (day/month/year) 22 April 1999 (22.04.99)	**Priority date** (day/month/year) 22 April 1998 (22.04.98)
Applicant CRAIG, Hugh, Patrick et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

18 November 1999 (18.11.99)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Juan Cruz

Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION** see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
HL58057/003/WS.		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/GB 99/ 01236	22/04/1999	22/04/1998
Applicant		
MULTICORE SOLDERS LIMITED.et.al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 03 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

[ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

[ ] contained in the international application in written form.

[ ] filed together with the international application in computer readable form.

[ ] furnished subsequently to this Authority in written form.

[ ] furnished subsequently to this Authority in computer readble form.

[ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

[ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

[X] the text is approved as submitted by the applicant.

[ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

[X] the text is approved as submitted by the applicant.

[ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. ---

[ ] as suggested by the applicant.

[ ] because the applicant failed to suggest a figure.

[ ] because this figure better characterizes the invention.

[ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/01236

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G59/18 H01L21/56 B23K35/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 07542 A (KIRSTEN KENNETH J) 27 February 1997 (1997-02-27) page 31, line 36 - page 32, line 30; claims; example 7	1-42
X	WO 97 07541 A (KIRSTEN KENNETH J) 27 February 1997 (1997-02-27) claims	1-42
X	WO 98 08362 A (CRAIG HUGH P) 26 February 1998 (1998-02-26) claims	1-42
X	WO 93 06943 A (TORANAGA TECHNOLOGIES INC) 15 April 1993 (1993-04-15) claims	1-42

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 August 1999	09/09/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Deraedt, G

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/01236

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
P,X	CHEMICAL ABSTRACTS, vol. 130, no. 21, 24 May 1999 (1999-05-24) Columbus, Ohio, US; abstract no. 289696, JOHNSON, R.W., E.A.: "Reflow-curable polymer fluxes for flip chip encapsulation" XP002113667 abstract & PROC. - INT. CONF. MULTICHIP MODULES HIGH DENSITY PACKAG.,1998, pages 41-45,	1-42

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 99/01236

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9707542 A	27-02-1997	EP 0870329 A	14-10-1998
		EP 0843894 A	27-05-1998
		WO 9707541 A	27-02-1997
WO 9707541 A	27-02-1997	EP 0870329 A	14-10-1998
		EP 0843894 A	27-05-1998
		WO 9707542 A	27-02-1997
WO 9808362 A	26-02-1998	AU 3781797 A	06-03-1998
		EP 0933010 A	04-08-1999
WO 9306943 A	15-04-1993	US 5376403 A	27-12-1994
		AU 663342 B	05-10-1995
		AU 2767892 A	03-05-1993
		CA 2120523 A	15-04-1993
		EP 0646048 A	05-04-1995
		JP 7502369 T	09-03-1995
		KR 9710170 B	21-06-1997
		MX 9205644 A	31-08-1994
		US 5538789 A	23-07-1996
		US 5830389 A	03-11-1998
		US 5565267 A	15-10-1996
		US 5716663 A	10-02-1998
		US 5853622 A	29-12-1998

PATENT COOPERATION TREATY

REC'D 07 JUL 2000
WIPO PCT

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
HL58057/003/WS		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/GB99/01236	22/04/1999	22/04/1998
International Patent Classification (IPC) or national classification and IPC C08G59/18		
Applicant MULTICORE SOLDERS LIMITED et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 21 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
18/11/1999	05.07.2000
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Gordon. M Telephone No. +49 89 2399 8299

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/01236

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-14	as received on	13/06/2000	with letter of	08/06/2000

Claims, No.:

1-42	as received on	13/06/2000	with letter of	08/06/2000

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

☒ the entire international application.

☐ claims Nos. .

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):

☒ the claims, or said claims Nos. 1,37 are so inadequately supported by the description that no meaningful opinion could be formed.

☐ no international search report has been established for the said claims Nos. .

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	See Comments
	No:	Claims	
Inventive step (IS)	Yes:	Claims	See Comments
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-42
	No:	Claims	

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

1). The amendments filed do not comply with the requirements of Art 34(2)b PCT. The definition of the curing temperature lying between liquidus temperatures of two - albeit conventionally employed - types of solder is not derivable from the specification as originally filed. There is further no statement that would link the originally employed - unclear - term "soldering temperatures" to a range between these two points.

The subject matter of claim 36 extends beyond the disclosure of the original application. The feature "..curable when the material of the solder bump is molten.." is not disclosed or derivable in any manner from the original specification.
The final feature of this claim is also questionable. Although the phenomena by which metal oxides removed from the surface contributes to curing is discussed in the application (page 3 line 20ff) this is presented as an unwanted phenomena, in causing premature cure. Accordingly it is not admissible now to present this as a desired part of the method.

These objections apply also to the corresponding parts of the description.

2). In view of the formal inadmissibility of the two independent claims, formulation of an opinion on the question of novelty and inventive step is not possible.

However, for the sake of completeness, the following comments and provisional conclusions are presented.

WO97/07542 discloses in example 1 a composition containing a bisphenol A epoxy resin, an anhydride and a tertiary amine as catalyst. This discloses in example 1 that cure of the composition cures starts below the melting point of the solder. However, this does not mean that curing does not continue **at** the melting point of the solder. It is also apparent that this composition will be storage stable without the catalyst. The fact that the composition, with the catalyst exhibits poor stability is in the nature of including a catalyst and cannot affect this conclusion. This disclosure thus anticipates the subject matter of claims 1-4,7-11,14,22-26, the formal deficiencies notwithstanding. This composition is employed as a solder paste particularly in the surface- mounting process, with the result that the subject

matter of claims 36-42 is also anticipated.
Similar conclusions are reached in view of the disclosure of WO97/07541, W=98/08362 and WO93/06943 (page 22ff).

2). The subject matter of claim 16 is distinguished from the above teachings by the presence of an additional acid flux. It appears that the use of such fluxes, in particular in view of the inhibition of curing is conventional. Further no technical effect has been shown to derive from this feature. Hence no inventive step can be acknowledged for this feature.
The subject matter of claim 27 is distinguished from the above teachings by the presence of a filler. It is conventional practice to include fillers in adhesive compositions. As in the case of the acid flux agent, no technical effect has been evidenced to derive from this feature. Accordingly no inventive step is recognised.

ADHESIVE AND ENCAPSULATING MATERIAL WITH FLUXING PROPERTIES AND USE THEREOF IN UNDERFILL TECHNOLOGY

This invention relates to electrical interconnection methods in electronic circuitry and more particularly to flip chip attachment and encapsulation of both naked semi-conductors and chip scale packages (CSPs). The technology is commonly referred to as underfill technology.

As is noted in US-A-5 128 746, solder bump interconnections when attaching chips to electronic circuitry eliminate the expense, performance limitations, low productivity and poor space utilisation of wire bonding. As circuit density increases occur, while circuit board and assembly sizes continue to shrink, so-called flip-chip interconnection using solder bumps has proved to be the most suitable technique for satisfying such demands.

With the most common form of flip-chip interconnection, solder bumps are placed on terminals of the integrated circuit being produced while the substrate for the integrated circuit is still in the form of a small wafer or die. Commonly, the eutectic Sn/Pb 60/40 or a high melting point alloy such as Sn/Pb 3/97, which is known to have been employed in the IBM C4 process, is employed as solder material. The die or wafer carrying the integrated circuit is to be joined to a substrate and for this purpose the die or wafer will be inverted (hence the term flip-chip). It is current manufacturing practice to place a flux or solder paste on the substrate. This material will promote the adhesion of the die to the substrate during reflow of the solder bump. During reflow, the assembly produced is subjected to a temperature sufficient to melt or collapse (C4 process) the solder bump and form

the required interconnections. The flux residue must then be removed to prevent corrosion occurring to the die and, importantly, to allow free ingress of a subsequent underfill resin which is to encapsulate the various semi-conductors of the electronic circuitry produced.

For this latter purpose, an underfill encapsulant resin is applied around and under the die following reflow and flux removal. The very small gap between the die and substrate must be completely filled in order to provide environmental protection for the device. The filling of this gap is dependent on capillary action of the encapsulant material between the integrated circuit and substrate. The filling of the gap has proved to be a procedure which is very time consuming, expensive and difficult to achieve in the desired quality and is generally an unreliable procedure, particularly when a relatively large die is used. Moreover, the low viscosity of encapsulant material needed to ensure capillary action runs counter to the need to control thermal expansion and thermal conductivity by filling the encapsulation resin with ceramic powder which generally increases the viscosity of the resin. A solution to this problem has been to heat the substrate/component assembly to reduce initially the viscosity of the underfilling encapsulant resin. Temperatures must be precisely controlled and the process is difficult to control since the elevated temperature triggers the curing mechanism thus raising viscosity prematurely. For these various reasons, the underfilling process currently employed has low productivity and high space/equipment needs.

In the aforementioned US-A-5 128 746, it is proposed to add a fluxing agent to a cross-linking agent - containing encapsulant resin, the encapsulant resin being dispensed onto the substrate before the

integrated circuit-carrying chip is placed in the encapsulant resin for reflow. US-A-5 128 746 discloses the use of certain strong organic dicarboxylic acids as examples of commercially available fluxing agents. A fluxing encapsulant resin of such type has three very serious drawbacks which compromise the integrity of the interconnection. Free acid remains in the encapsulant after reflow and can and will attack and corrode metal present, especially on the die or wafer. This problem is exacerbated by the decreased environmental resistance of such adhesive composition due to the presence of unreacted resin. As the adhesive composition has relatively low resistance to humidity and moisture, the corrosion problem is thus intensified. Moreover, the addition of acids of the stated type to epoxy resin adhesives compromises the stability of the adhesive, greatly reducing pot life and making cure characteristics variable. This will have a major effect on reliability and process control.

Finally, it is known that salts formed during fluxing of materials by reaction between metal oxides and fluxing agent and containing various metals including tin and lead can have a catalytic action on polymer materials thus causing a premature cure of the polymer prior to reflow of the solder.

It is an object of this invention to provide for the use of a thoroughly curable adhesive which does not suffer the problem of unreacted acid remaining in the encapsulant after reflow or the problem of pre-cure of the polymer due to salts formed during fluxing.

In one aspect, this invention provides a thermally curable adhesive composition which comprises:

(a) a thermosetting polymer, or a monomer which is polymerisable to yield a thermosetting polymer, said polymer being crosslinkable when subject to the action of a chemical crosslinking agent; and

(b) a chemical crosslinking agent for said polymer, the crosslinking agent having fluxing properties and exhibiting no reactivity, or exhibiting very restricted reactivity with the polymer without the action of a catalyst and/or heat; and

which composition is thermally curable when heated to temperature range extending from the liquidus temperature of the alloy Sn/Pb 60/40 up to the liquidus temperature of the alloy Sn/Pb 3/97 and in the presence of a catalyst for the crosslinking of the polymer with a crosslinking agent and is storage and reaction stable in the absence of such catalyst and at temperatures in the range of from 20-25°C.

According to a second aspect of the present invention there is provided a method of producing an electronic device which comprises opposing an electrical component having a surface carrying a plurality of electrical terminations, each termination including a solder bump, and a component-carrying substrate having a plurality of electrical terminations corresponding to the terminations of the electrical component, with a thermally curable adhesive composition being applied to said surface of the electrical component and/or to the substrate, bringing the electrical component and substrate into contact at elevated temperature and thereby soldering the electrical component to the substrate and simultaneously achieving encapsulation thereof in thermoset polymer produced in situ from monomer or polymer in the adhesive composition, in which method (1) the thermally curable adhesive composition comprises:

(a) a thermosetting polymer, or a monomer which is polymerisable to yield a thermosetting polymer, said polymer being crosslinkable when subject to

the action of a chemical crosslinking agent; and

(b) a chemical crosslinking agent for said polymer, the crosslinking agent having fluxing properties and exhibiting no reactivity, or exhibiting very restricted reactivity with the polymer without the action of a catalyst and/or heat; and

which composition is thermally curable when the material of the solder bump is molten and in the presence of a catalyst for the crosslinking of the polymer with the crosslinking agent and is storage and reaction stable in the absence of such catalyst and at temperatures in the range of 20-25°C and (2) catalysis of crosslinking of the thermally curable adhesive is achieved by metal oxide removed from metal surfaces by the fluxing composition and/or salts formed by reaction between metal oxide and crosslinking agent.

This method uses novel adhesive compositions which are preferably compositions of the first aspect of the present invention.

A crosslinking agent to be employed in the practice of the present invention will have fluxing properties so as to enable it to remove oxides from the material with which it is in contact, i.e. die and substrate metallisation and, more particularly, solder metal, thereby allowing solder joint formation. The crosslinking agent, when present in sufficient amount, is to be capable of complete reaction with thermosetting polymer to neutralise, i.e. react with all reaction sites of the polymer. The design of the adhesive is preferably intended to ensure absence of residual cross-linking agent therein and hence equimolar quantities of polymer and crosslinking agent are generally used. However, excess cross-linking agent is not a problem in the practice of this invention. Although it has the potential to corrode

metal surfaces which are normally accessible via pinholes which are present unavoidably in resin, now any excess cross-linking agent remains trapped in the polymer matrix together with catalyst so that corrosion of metal is not a problem. The composition itself is storage and reaction stable until heated to a temperature at which the latent reaction catalyst effectively causes the crosslinking agent to cure the thermosetting polymer and at which temperature the crosslinking agent will have melted and dissolved in the polymer or monomer.

Thus, the present invention provides for the use of chip underfill and encapsulation adhesive compositions having fluxing properties which enable one to achieve overall a rugged structure with protection of integrated circuits which have been previously solder bumped and then flip chip connected to a substrate with a metallisation pattern. During reflow, the fluxing achieved with the crosslinking agent allows metallic interconnection to be achieved between solder bump and metallisation pads on the substrate. The adhesive composition then reacts and cures to provide a fully adhered encapsulate underfill that is non-corrosive and environmentally resistant. The adhesive compositions themselves are stable and provide a long storage life at ambient temperatures, that is 20-25°C, while maintaining predictable processing characteristics. The adhesive compositions lack the substantial debilitating defects in the hitherto known compositions by providing a means for predepositing the underfill and eliminating separate fluxing and cleaning. The adhesive composition may be modified to optimise CTE, glass transition temperature (Tg), elasticity modulus and thermal conductivity without detriment to the aforementioned benefits or detriment to the require rheological properties which allow for

ease of deposition, for example by syringe dispensing. In addition, curing is achieved readily during any suitable thermal treatment, for example during reflow soldering. The underfill may only be partially cured after one or several solder reflow cycles, thus enabling ease of reworking of the device. Full cure is then achieved in a separate post-cure heat application. Alternatively, full cure may be obtained from one or two reflow cycles if reworkability is not required.

Insofar as the solder is concerned, this may consist of one or more metals which provide a suitable low melting point material. The metals employed are typically selected from tin, lead, bismuth, cadmium, zinc, gallium, indium, tellurium, mercury, thallium, antimony and selenium. The preferred such metal is tin or a tin/lead alloy. Specific examples of solders which may be employed are the aforementioned eutectic Sn/Pb 60/40 and the high melting point Sn/Pb 3/97.

The thermosetting polymer or monomer utilised in the compositions employed in the method of this invention is an adhesive substance which is preferably liquid at ambient temperature. Thus one may utilise a reactive polyester or an epoxide monomer or polymer such as an epoxy Novolak or epoxide precursor thereof. A preferred epoxy resin is either a diglycidyl ether of bisphenol A or a diglycidyl ether of bisphenol F. In preferred practice, such an epoxy resin is a B-stage resin or a resin which may be "B-staged" after application, thereby making it possible for there to be a delay before bringing together the component and the substrate. Other preferred epoxy materials to use are substances from the Araldite series of Ciba-Geigy Resins, such as the trifunctional epoxide MY10510 and the difunctional cycloaliphatic epoxide ERL 4221 which may be used singly or in admixture. The Araldite MY10510 may be replaced by Aradite MY9512, a tetra-

functional epoxide-based resin. MY9512 may be used alone, too, as may the trifunctional epoxide-based resin MY10510. The composition of the invention may also contain a monomer precursor for a polymer, e.g. an epoxide compound when an epoxy resin is required. Mixtures of such epoxy materials may also be used.

The crosslinking agent with fluxing properties is usually solid at ambient temperature, but, provided it meets the reactivity requirements set out above for crosslinking agents of adhesive composition to be used this invention, it can also be liquid at ambient temperatures. The crosslinking agent is preferably a di-or polycarboxyl compound which is unreactive at ambient temperature and insoluble in the monomer or polymer until heated, in practice generally to soldering temperatures, and such cross linking agents are generally referred to hereafter as polyacids. The cross-linking agent is preferably solid for this reason. Such polyacids serve as a fluxing agent for the oxide material present on the solder, which metal oxide is a catalyst for reaction between an epoxy resin and the carboxyl groups of the polymer at elevated temperatures. Such polyacid may be in particular a carboxylated polymer, a multifunctional polyanhydride or a long chain (C_8 or greater, preferably C_{10} or greater) polycarboxylic acid, preferably dicarboxylic acid. These acidic reactive compounds having a functionality greater than 1 provide multiple reaction sites, with epoxy resin serving to create a macromolecule that provides adhesion. A particularly preferred example of a polymer containing two or more carboxyl groups which may be employed is a styrene-acrylic acid copolymer. A preferred dicarboxylic acid is dodecanedioic acid (DDDA).

The polyanhydrides which may be used as cross-linking agent with fluxing properties in the practice

of this invention and which are preferably solid include polyazelaic polyanhydride and polyadipic polyanhydride. These materials provide stability when and mixed with epoxy resin and become active fluxing and curing agents only when heated to their melting points.

Other crosslinking agents with fluxing properties which can be used are mono, di-and polyhydrazides which are solid at ambient temperature and insoluble in the monomer or polymer until heated, in practice generally to soldering temperature. A preferred such compound is adipic dihydrazide. Because of the differing reactivities of polycarboxylic acids and hydrazides, it is preferred to use a mixture of crosslinking agents, such as dodecanedioic acid and adipic dihydrazide, the higher reactivity of the latter being countered by the lower reactivity of the former.

While the oxide removed from the solder or a salt produced by reaction between the polyacid and such oxide, as a result of the fluxing activity of the crosslinking agent, acts as a catalyst for the curing of the polymer, curing in the manner of a snap cure fix is achieved only when a catalyst is present, such catalyst being active at the elevated temperature utilised for soldering. A preferred such latent catalyst is an imidazole catalyst especially phenyl imidazole. This effect is often not desirable as it is contrary to the need to adjust positioning of components during soldering. Other latent reaction catalysts which can be used are tertiary amines with the amine groups optionally substituting the reactive monomer or polymer, as in the aforesaid Araldite MY10510 or MY9512, or metallic salts such as tin octanoate, dibutyl tin dilaurate, ferric acetylacetonate, and cobalt (III) acetylacetonate.

Preferred compositions will have a thermosetting

polymer-crosslinking agent/flux content in which there are from 45 to 70%, more preferably 50 to 60%, by weight of thermosetting polymer and from 55 to 30% by weight, more preferably 50 to 40%, by weight crosslinking agent/flux.

The use in adhesive compositions employed for encapsulating flip chip connections of ceramic powders to enhance thermal expansion and modulus properties of the composition is preferably to be adopted in the practice of the present invention. It is preferred that such ceramic powders be highly thermally conductive to enhance the connection between solder bump and conductor on the substrate while ensuring that the compositions retain the low viscosity necessary for fluxing and for ease of deposition. The filler is preferably a nominally 5μ diameter spherical ceramic bead or hollow sphere composition. More generally, it may be a glass or ceramic powder comprising spherical particles of 0.1-25μ, preferably 1-15μ, diameter or comprise essentially monodisperse spherical particles having a single diameter of 0.1-25μ, preferably 1-15μ. The ceramic powder has preferably a very high thermal conductivity. Examples of such ceramic powders which may be employed are SiO_2, MgO, Al_2O_3, TiO_2/ZnO, barium sulphate and diamond dust. In some cases, it is preferred that the ceramic powder utilised has instead a very low or negative coefficient of thermal expansion, too, and if this requirement is imposed on the ceramic powder then a preferred example is aluminium lithium silicate.

Metal oxides formed on solder metals even at ambient temperatures are themselves a problem since they can catalyse crosslinking of the thermosetting resin or its monomer precursor. In accordance with a preferred embodiment of the invention, the resin or precursor contains an acid flux which is liquid at

temperatures below 100°C, preferably below 40°C, more preferably ambient temperature. This acid will react with oxides to form salts which will not decompose until at elevated temperatures, in particular soldering temperatures when the resulting oxides, together with oxides formed on the metal surfaces more readily at the higher temperatures and removed from the metal surfaces by the flux/crosslinking agent, will catalyse the crosslinking of the thermosetting polymer.

The term "acid" as such is used herein to denote the more volatile flux for preventing prepolymerisation/crosslinking and to distinguish it from the solid crosslinking agent/flux. The more volatile flux is generally liquid at ambient temperature so that it acts immediately as a flux. It should certainly be liquid, at least at temperatures below those at which the crosslinking agents used become fully reactive in the presence of metal oxide/salt crosslinking catalysts. It is thus preferred that the acid used for preventing prepolymerisation, even if solid at ambient temperature, is liquid by 40°C.

Such liquid acids may be polyacids, but will normally be monocarboxylic acids. The acids preferably contain at least 8 carbon atoms and are exemplified by versatic acids, in particular versatic 10 which is a synthetic acid composed of a mixture of highly branched isomers of C_{10} monocarboxylic acids, mainly of tertiary structure. The high degree of branching gives rise to steric hindrance which means that the salts formed are thoroughly stable and difficult to break down. Other acids which may be used are capric acid, caprylic lauric acid, stearic acid and palmitic acid.

When such monocarboxylic acids are to be used, compositions embodying the invention preferably will have a thermosetting polymer - flux content in which

there are 30 to 70%, more preferably 50 to 60%, by weight of thermosetting polymer and from 70 to 30%, more preferably 50 to 40%, by weight of a mixture of fluxes, the flux components consisting of from 80 to 97%, preferably 85 to 95%, by weight of solid crosslinking agent/flux and from 20 to 3%, preferably 15 to 5%, by weight of acid flux which is liquid at below 100°C.

When practising the present invention, there is no need for the adhesive composition to be introduced subsequent to formation of a solder connection with the attendant difficulties identified above. It is possible for the composition to be predeposited, before emplacement and soldering of electronic component to substrate, on either or both of the electronic component and the substrate. As there is no need for a separate fluxing agent to be employed which is not incorporated in the adhesive composition, the presence of the composition on one or other of the electronic component and the substrate fulfils the required fluxing function. Insofar as the composition may be applied to the electronic component, then application may be to dies which are either in wafer form or as separate discrete devices. Application of the composition may be by screen printing, stencil printing, dispensing, spinning or any other known method for applying a composition to discrete areas.

The ease of working in accordance with the method of this invention enables the composition to contain the thermosetting resin in the form of a B-stageable precursor for application to die, substrate or carrier tape and then B-staging so as to form a handleable film which becomes fully crosslinked only when the soldering operation is carried out.

The following examples illustrate the adhesive compositions which may be used in the practice of this

invention. In the examples all percentages are percentages by weight.

Example 1

ERL 4221	40.6%
MY9512	12.7%
DDDA	46.7%

This composition was functionally good and of satisfactory viscosity for most applications.

Example 2

ERL 4221	39.65%
Epoxy MY9512	12.40%
DDDA	41.05%
Versatic 10	6.90%

This composition was functionally good in not undergoing pre-crosslinking but had too low a viscosity for some applications. As a result, higher viscosity compositions as follows were made up and found to work well.

Example 3

ERL 4221	33.45%
MY9512	18.60%
DDDA	41.05%
Versatic 10	6.90%

Example 4

ERL 4221	26.05%
MY9512	26.00%
DDDA	41.05%
Versatic 10	6.90%

Example 5

ERL 4221	12.40%
MY9512	39.65%
DDDA	41.05%

Versatic 10 6.90%

The initial viscosity of the composition is here somewhat too high for ease of use. Moreover, while Examples 2 to 5 made use of monocarboxylic acids liquid at ambient temperature, it is also possible to use monocarboxylic acids solid at ambient temperature but liquid at temperatures below those at which the crosslinking agent/flux are, for example, as follows:-

Example 6		
ERL 4221	39.65%	
Epoxy MY9512	12.40%	
DDDA	41.05%	
Prifrac 2960	6.90%	(C16 Palmitic acid - solid melts at 60°C)
Example 7		
ERL 4221	39.65%	
Epoxy MY9512	12.40%	
DDDA	41.05%	
Versatic 10	6.90%	(C18 - melts at 69°C)

Finally compositions were formulated which contained lower amounts of monocarboxylic acid. These, too, proved to be satisfactory.

Example 8	
ERL 4221	39.65%
MY9512	12.40%
DDDA	44.95%
Versatic 10	3.00%
Example 9	
ERL 4221	42.62%
MY9512	13.33%
DDDA	41.05%
Versatic 10	3.00%

CLAIMS

1. A thermally curable adhesive composition which comprises:

(a) a thermosetting polymer, or a monomer which is polymerisable to yield a thermosetting polymer, said polymer being crosslinkable when subject to the action of a chemical crosslinking agent; and

(b) a chemical crosslinking agent for said polymer, the crosslinking agent having fluxing properties and exhibiting no reactivity, or exhibiting very restricted reactivity with the polymer without the action of a catalyst and/or heat; and

which composition is thermally curable when heated to temperature range extending from the liquidus temperature of the alloy Sn/Pb 60/40 up to the liquidus temperature of the alloy Sn/Pb 3/97 and in the presence of a catalyst for the crosslinking of the polymer with a crosslinking agent and is storage and reaction stable in the absence of such catalyst and at temperatures inthe range of from 20-25°C.

2. A composition according to claim 1, wherein the chemical crosslinking agent is solid at ambient temperature.

3. A composition according to claim 2, wherein said chemical crosslinking agent is selected from polyacids, polyanhydrides and hydrazides which are insoluble in the monomer or polymer until heated to soldering temperature.

4. A composition according to claim 3, wherein the polyacid is selected from polymers containing two or more carboxyl groups and di- and polycarboxylic acids and di-and polyanhydrides..

5. A composition according to claim 4, wherein the polycarboxylic acid is a C_8 or greater dicarboxylic acid.

6. A composition according to claim 3, wherein the hydrazide is a monohydrazide, dihydrazide or polyfunctional hydrazide.

7. A composition according to any one of claims 3 to 6, wherein the crosslinking agent contains a dihydrazide and/or a dicarboxylic acid.

8. A composition according to claim 7, wherein the crosslinking agent contains adipic dihydrazide and/or dodecanedioic acid.

9. A composition according to claim 4, wherein the crosslinking agent is a styrene acrylic acid copolymer.

10. A composition according to any preceding claim, which has a thermosetting polymer - solid crosslinking agent/flux content in which there are from 30 to 70% by weight of thermosetting polymer and from 70 to 30% by weight of solid crosslinking agent/flux.

11. A composition according to Claim 10, wherein said thermosetting polymer content is from 50 to 60% by weight and said solid crosslinking agent/flux content is from 50 to 40% by weight of the total amount of thermosetting polymer and crosslinking agent/flux.

12. A composition according to any one of claims 1 to 11, wherein said polymer is an epoxy resin.

13. A composition according to claim 12, wherein said polymer is a B-staged epoxy resin.

14. A composition according to claim 13, wherein the said polymer is a diglycidyl ether of bisphenol A.

15. A composition according to claim 14, wherein the said polymer is based on a tri- or tetrafunctional epoxide or a difunctional cycloaliphatic epoxide or a mixture of two or more such epoxides.

16. A composition according to any preceding claim, which additionally comprises an acid flux which is liquid at temperatures below 100°C.

17. A composition according to Claim 16, wherein the acid flux is liquid at temperatures of from 20 to 25°C.

18. A composition according to Claim 16 or 17, wherein the acid flux is a monocarboxylic acid, preferably containing at least 8 carbon atoms.

19. A composition according to Claim 18, wherein the acid flux is a versatic acid, capric acid, caprylic acid, lauric acid, stearic acid or palmitic acid.

20. A composition according to any one of Claims 16 to 19, which has a thermosetting polymer-flux content in which there are from 30 to 70% by weight of thermosetting polymer and from 70 to 30% by weight of flux, which flux is, in turn, made up from 80 to 97% by weight of said solid crosslinking agent/acid flux and from 20 to 3% by weight of said acid flux.

21. A composition according to Claim 20, which has a thermosetting polymer-flux content in which there are from 50 to 60% by weight of thermosetting polymer and from 50 to 40% by weight of flux, which flux is, in turn, made up from 85 to 95% by weight of said solid

crosslinking agent/flux and from 15 to 5% by weight of said acid flux.

22. A composition according to any preceding claim, which additionally comprises a latent reaction catalyst selected from tertiary amines and imidazoles and metallic salts.

23. A composition according to Claim 22, wherein the imidazole is phenyl imidazole.

24. A composition according to Claim 22, wherein the tertiary amine is constituted by self catalysing tertiary amine groups substituting the reactive monomer or polymer.

25. A composition according to Claim 24, wherein the reactive monomer is a tertiary amine-substituted trifunctional or tetrafunctional epoxide.

26. A composition according to Claim 22, wherein the metallic salt is tin octanoate, dibutyl tin dilaurate, ferric acetylacetonate, and cobalt (III) acetylacetonate.

27. A composition according to any preceding claim which further comprises a thermally conductive filler.

28. A composition according to Claim 27, wherein said filler reduces thermal expansion of the composition.

29. A composition according to Claims 27 and 28, wherein the filler is constituted by nominally 5μ spherical ceramic beads or hollow spheres.

30. A composition according to Claim 27, wherein the

filler is a ceramic or glass ceramic powder comprising spherical particles with diameters in the range from 0.1 to 25μ, preferably 1-15μ.

31. A composition according to Claim 27, wherein the filler is a ceramic or glass ceramic powder consisting essentially of monodisperse spherical particles having a single diameter in the range from, 0.1 to 25μ, preferably 1-15μ.

32. A composition according to Claim 27, wherein the filler is a thermally conductive ceramic powder.

33. A composition according to Claim 32, wherein the ceramic powder is selected from SiO_2, MgO, Al_2O_3, TiO_2 /ZnO, barium sulphate and diamond dust.

34. A composition according to Claim 27, wherein the ceramic powder has a negative coefficient of thermal expansion.

35. A composition according to Claim 34, wherein the ceramic material is aluminium lithium silicate.

36. A method of producing an electronic device which comprises opposing an electrical component having a surface carrying a plurality of electrical terminations, each termination including a solder bump, and a component-carrying substrate having a plurality of electrical terminations corresponding to the terminations of the electrical component, with a thermally curable adhesive composition being applied to said surface of the electrical component and/or to the substrate, bringing the electrical component and substrate into contact at elevated temperature and thereby soldering the electrical component to the

substrate and simultaneously achieving encapsulation thereof in thermoset polymer produced in situ from monomer or polymer in the adhesive composition, in which method (1) the thermally curable adhesive composition comprises:

(a) a thermosetting polymer, or a monomer which is polymerisable to yield a thermosetting polymer, said polymer being crosslinkable when subject to the action of a chemical crosslinking agent; and

(b) a chemical crosslinking agent for said polymer, the crosslinking agent having fluxing properties and exhibiting no reactivity, or exhibiting very restricted reactivity with the polymer without the action of a catalyst and/or heat; and

which composition is thermally curable when the material of the solder bump is molten and in the presence of a catalyst for the crosslinking of the polymer with the crosslinking agent and is storage and reaction stable in the absence of such catalyst and at temperatures in the range of 20-25°C and (2) catalysis of crosslinking of the thermally curable adhesive is achieved by metal oxide removed from metal surfaces by the fluxing composition and/or salts formed by reaction between metal oxide and crosslinking agent.

37. A method as claimed in Claim 36, wherein the thermally curable adhesive composition is applied to one and/or both of the said electrical component and said substrate prior to bringing the two together.

38. A method as claimed in Claim 36 or 37, wherein no fluxing agent is applied to either the surface of said electrical component carrying the electrical terminations or to said substrate prior to application of the curable adhesive composition.

39. A method as claimed in any one of Claims 36 to 38, wherein the thermally curable adhesive composition is applied to dies, which are either in wafer form or as separate discrete devices.

40. A method as claimed in any one of Claims 36 to 39, wherein the thermally curable adhesive composition is applied by screen printing, stencil printing, dispensing or spinning.

41. A method as claimed in any one of claims 36 to 40, wherein the thermally curable adhesive composition is a composition as claimed in any one claims 1 to 35.

42. A method as claimed in any one of Claims 36 to 41, wherein the thermally curable adhesive composition is applied in B-stageable form and B-staged in situ.

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

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PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing *(day/month/year)*	05.07.2000
Applicant's or agent's file reference HL58057/003/WS	**IMPORTANT NOTIFICATION**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/GB99/01236	22/04/1999	22/04/1998

Applicant
MULTICORE SOLDERS LIMITED et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

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Form PCT/IPEA/416 (July 1992)

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of Internationa Preliminary Examination Report (Form PCT/II
HL58057/003/WS		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/GB99/01236	22/04/1999	22/04/1998

International Patent Classification (IPC) or national classification and IPC
C08G59/18

Applicant
MULTICORE SOLDERS LIMITED et al.

1. This international preliminary examination report has been prepared by this International Preliminary Examinin and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings whicl been amended and are the basis for this report and/or sheets containing rectifications made before this Au (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 21 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicabil citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
18/11/1999	05.07.2000

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/01236

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-14	as received on	13/06/2000	with letter of	08/06/2000

Claims, No.:

1-42	as received on	13/06/2000	with letter of	08/06/2000

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

☒ the entire international application.

☐ claims Nos. .

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):

☒ the claims, or said claims Nos. 1.37 are so inadequately supported by the description that no meaningful opinion could be formed.

☐ no international search report has been established for the said claims Nos. .

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	See Comments
	No:	Claims	
Inventive step (IS)	Yes:	Claims	See Comments
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-42
	No:	Claims	

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

1). The amendments filed do not comply with the requirements of Art 34(2)b PCT. The definition of the curing temperature lying between liquidus temperatures of two - albeit conventionally employed - types of solder is not derivable from the specification as originally filed. There is further no statement that would link the originally employed - unclear - term "soldering temperatures" to a range between these two points.

The subject matter of claim 36 extends beyond the disclosure of the original application. The feature "..curable when the material of the solder bump is molten.." is not disclosed or derivable in any manner from the original specification.
The final feature of this claim is also questionable. Although the phenomena by which metal oxides removed from the surface contributes to curing is discussed in the application (page 3 line 20ff) this is presented as an unwanted phenomena, in causing premature cure. Accordingly it is not admissible now to present this as a desired part of the method.

These objections apply also to the corresponding parts of the description.

2). In view of the formal inadmissibility of the two independent claims, formulation of an opinion on the question of novelty and inventive step is not possible.

However, for the sake of completeness, the following comments and provisional conclusions are presented.

WO97/07542 discloses in example 1 a composition containing a bisphenol A epoxy resin, an anhydride and a tertiary amine as catalyst. This discloses in example 1 that cure of the composition cures starts below the melting point of the solder. However, this does not mean that curing does not continue **at** the melting point of the solder. It is also apparent that this composition will be storage stable without the catalyst. The fact that the composition, with the catalyst exhibits poor stability is in the nature of including a catalyst and cannot affect this conclusion. This disclosure thus anticipates the subject matter of claims 1-4,7-11,14,22-26, the formal deficiencies notwithstanding. This composition is employed as a solder paste particularly in the surface- mounting process, with the result that the subject

matter of claims 36-42 is also anticipated.
Similar conclusions are reached in view of the disclosure of WO97/07541, W=98/08362 and WO93/06943 (page 22ff).

2). The subject matter of claim 16 is distinguished from the above teachings by the presence of an additional acid flux. It appears that the use of such fluxes, in particular in view of the inhibition of curing is conventional. Further no technical effect has been shown to derive from this feature. Hence no inventive step can be acknowledged for this feature.
The subject matter of claim 27 is distinguished from the above teachings by the presence of a filler. It is conventional practice to include fillers in adhesive compositions. As in the case of the acid flux agent, no technical effect has been evidenced to derive from this feature. Accordingly no inventive step is recognised.

ADHESIVE AND ENCAPSULATING MATERIAL WITH FLUXING PROPERTIES

This invention relates to electrical interconnection methods in electronic circuitry and more particularly to flip chip attachment and encapsulation of both naked semi-conductors and chip scale packages (CSPs). The technology is commonly referred to as underfill technology.

As is noted in US-A-5 128 746, solder bump interconnections when attaching chips to electronic circuitry eliminate the expense, performance limitations, low productivity and poor space utilisation of wire bonding. As circuit density increases occur, while circuit board and assembly sizes continue to shrink, so-called flip-chip interconnection using solder bumps has proved to be the most suitable technique for satisfying such demands.

With the most common form of flip-chip interconnection, solder bumps are placed on terminals of the integrated circuit being produced while the substrate for the integrated circuit is still in the form of a small wafer or die. Commonly, the eutectic Sn/Pb 60/40 or a high melting point alloy such as Sn/Pb 3/97, which is known to have been employed in the IBM C4 process, is employed as solder material. The die or wafer carrying the integrated circuit is to be joined to a substrate and for this purpose the die or wafer will be inverted (hence the term flip-chip). It is current manufacturing practice to place a flux or solder paste on the substrate. This material will promote the adhesion of the die to the substrate during reflow of the solder bump. During reflow, the assembly produced is subjected to a temperature sufficient to melt or collapse (C4 process) the solder bump and form

the required interconnections. The flux residue must then be removed to prevent corrosion occurring to the die and, importantly, to allow free ingress of a subsequent underfill resin which is to encapsulate the various semi-conductors of the electronic circuitry produced.

For this latter purpose, an underfill encapsulant resin is applied around and under the die following reflow and flux removal. The very small gap between the die and substrate must be completely filled in order to provide environmental protection for the device. The filling of this gap is dependent on capillary action of the encapsulant material between the integrated circuit and substrate. The filling of the gap has proved to be a procedure which is very time consuming, expensive and difficult to achieve in the desired quality and is generally an unreliable procedure, particularly when a relatively large die is used. Moreover, the low viscosity of encapsulant material needed to ensure capillary action runs counter to the need to control thermal expansion and thermal conductivity by filling the encapsulation resin with ceramic powder which generally increases the viscosity of the resin. A solution to this problem has been to heat the substrate/component assembly to reduce initially the viscosity of the underfilling encapsulant resin. Temperatures must be precisely controlled and the process is difficult to control since the elevated temperature triggers the curing mechanism thus raising viscosity prematurely. For these various reasons, the underfilling process currently employed has low productivity and high space/equipment needs.

In the aforementioned US-A-5 128 746, it is proposed to add a fluxing agent to a cross-linking agent - containing encapsulant resin, the encapsulant resin being dispensed onto the substrate before the

integrated circuit-carrying chip is placed in the encapsulant resin for reflow. US-A-5 128 746 discloses the use of certain strong organic dicarboxylic acids as examples of commercially available fluxing agents. A fluxing encapsulant resin of such type has three very serious drawbacks which compromise the integrity of the interconnection. Free acid remains in the encapsulant after reflow and can and will attack and corrode metal present, especially on the die or wafer. This problem is exacerbated by the decreased environmental resistance of such adhesive composition due to the presence of unreacted resin. As the adhesive composition has relatively low resistance to humidity and moisture, the corrosion problem is thus intensified. Moreover, the addition of acids of the stated type to epoxy resin adhesives compromises the stability of the adhesive, greatly reducing pot life and making cure characteristics variable. This will have a major effect on reliability and process control.

Finally, it is known that salts formed during fluxing of materials by reaction between metal oxides and fluxing agent and containing various metals including tin and lead can have a catalytic action on polymer materials thus causing a premature cure of the polymer prior to reflow of the solder.

It is an object of this invention to provide a thoroughly curable adhesive which does not suffer the problem of unreacted acid remaining in the encapsulant after reflow or the problem of pre-cure of the polymer due to salts formed during fluxing.

According to one aspect of the present invention there is provided a thermally curable adhesive composition which comprises:

(a) a thermosetting polymer, or a monomer which is polymerisable to yield a thermosetting polymer, said polymer being crosslinkable when subject to

the action of a chemical crosslinking agent;

(b) a chemical crosslinking agent for said polymer, the crosslinking agent having fluxing properties and exhibiting no reactivity, or exhibiting very restricted reactivity with the polymer without the action of a catalyst and/or of heat; and

which composition is thermally curable when heated to soldering temperatures in the presence of a catalyst for the crosslinking of the polymer with a crosslinking agent and is storage and reaction stable in the absence of such catalyst and at ambient temperatures.

A crosslinking agent to be employed in the practice of the present invention will have fluxing properties so as to enable it to remove oxides from the material with which it is in contact, i.e. die and substrate metallisation and, more particularly, solder metal, thereby allowing solder joint formation. The crosslinking agent, when present in sufficient amount, is to be capable of complete reaction with thermosetting polymer to neutralise, i.e. react with all reaction sites of the polymer. The design of the adhesive is preferably intended to ensure absence of residual cross-linking agent therein and hence equimolar quantities of polymer and crosslinking agent are generally used. However, excess cross-linking agent is not a problem in the practice of this invention. Although it has the potential to corrode metal surfaces which are normally accessible via pinholes which are present unavoidably in resin, now any excess cross-linking agent remains trapped in the polymer matrix together with catalyst so that corrosion of metal is not a problem. The composition itself is storage and reaction stable until heated to a temperature at which the latent reaction catalyst effectively causes the crosslinking agent to cure the

thermosetting polymer and at which temperature the crosslinking agent will have melted and dissolved in the polymer or monomer.

Thus, the present invention provides chip underfill and encapsulation adhesive compositions having fluxing properties which enable one to achieve overall a rugged structure with protection of integrated circuits which have been previously solder bumped and then flip chip connected to a substrate with a metallisation pattern. During reflow, the fluxing achieved with the crosslinking agent allows metallic interconnection to be achieved between solder bump and metallisation pads on the substrate. The adhesive composition then reacts and cures to provide a fully adhered encapsulate underfill that is non-corrosive and environmentally resistant. The adhesive compositions themselves are stable and provide a long storage life at ambient temperatures, typically 20-25°C, while maintaining predictable processing characteristics. The adhesive compositions lack the substantial debilitating defects in the hitherto known compositions by providing a means for predepositing the underfill and eliminating separate fluxing and cleaning. The adhesive composition may be modified to optimise CTE, glass transition temperature (Tg), elasticity modulus and thermal conductivity without detriment to the aforementioned benefits or detriment to the require rheological properties which allow for ease of deposition, for example by syringe dispensing. In addition, curing is achieved readily during any suitable thermal treatment, for example during reflow soldering. The underfill may only be partially cured after one or several solder reflow cycles, thus enabling ease of reworking of the device. Full cure is then achieved in a separate post-cure heat application. Alternatively, full cure may be obtained from one or

two reflow cycles if reworkability is not required.

The invention thus also provides, in a second aspect, a method of producing an electronic device which comprises opposing an electrical component having a plurality of electrical terminations, each termination including a solder bump, and a component-carrying substrate having a plurality of electrical terminations corresponding to the terminations of the electrical component, with a thermally curable adhesive composition according to the first aspect of the invention being applied to a metal surface at one and/or both of said electrical component and said substrate, bringing the electrical component and substrate into contact at elevated temperature and thereby soldering the electrical component to the substrate and simultaneously achieving encapsulation thereof in thermoset polymer produced from said monomer or polymer in situ, catalysis of crosslinking of the thermally curable adhesive being achieved by metal oxide removed from metal surfaces by the fluxing composition and/or salts formed by reaction between metal oxide and crosslinking agent.

Insofar as the solder is concerned, this may consist of one or more metals which provide a suitable low melting point material. The metals employed are typically selected from tin, lead, bismuth, cadmium, zinc, gallium, indium, tellurium, mercury, thallium, antimony and selenium. The preferred such metal is tin or a tin/lead alloy. Specific examples of solders which may be employed are the aforementioned eutectic Sn/Pb 60/40 and the high melting point Sn/Pb 3/97.

The thermosetting polymer or monomer utilised in the compositions of this invention is an adhesive substance which is preferably liquid at ambient temperature. Thus one may utilise a reactive polyester or an epoxide monomer or polymer such as an epoxy

Novolak or epoxide precursor thereof. A preferred epoxy resin is either a diglycidyl ether of bisphenol A or a diglycidyl ether of bisphenol F. In preferred practice, such an epoxy resin is a B-stage resin or a resin which may be "B-staged" after application, thereby making it possible for there to be a delay before bringing together the component and the substrate. Other preferred epoxy materials to use are substances from the Araldite series of Ciba-Geigy Resins, such as the trifunctional epoxide MY10510 and the difunctional cycloaliphatic epoxide ERL 4221 which may be used singly or in admixture. The Araldite MY10510 may be replaced by Aradite MY9512, a tetra-functional epoxide. MY9512 may be used alone, too, as may the trifunctional epoxide MY10510. The composition of the invention may also contain a monomer precursor for a polymer, e.g. an epoxide compound when an epoxy resin is required. Mixtures of such epoxy materials may also be used.

The crosslinking agent with fluxing properties is usually solid at ambient temperature, but, provided it meets the reactivity requirements set out above for crosslinking agents of adhesive composition embodying this invention, it can also be liquid at ambient temperatures. The crosslinking agent is preferably a di-or polycarboxyl compound which is unreactive at ambient temperature and insoluble in the monomer or polymer until heated, in practice generally to soldering temperatures, and such cross linking agents are generally referred to hereafter as polyacids. The cross-linking agent is preferably solid for this reason. Such polyacids serve as a fluxing agent for the oxide material present on the solder, which metal oxide is a catalyst for reaction between an epoxy resin and the carboxyl groups of the polymer at elevated temperatures. Such polyacid may be in particular a

carboxylated polymer, a multifunctional polyanhydride or a long chain (C_8 or greater, preferably C_{10} or greater) polycarboxylic acid, preferably dicarboxylic acid. These acidic reactive compounds having a functionality greater than 1 provide multiple reaction sites, with epoxy resin serving to create a macromolecule that provides adhesion. A particularly preferred example of a polymer containing two or more carboxyl groups which may be employed is a styrene-acrylic acid copolymer. A preferred dicarboxylic acid is dodecanedioic acid (DDDA).

The polyanhydrides which may be used as cross-linking agent with fluxing properties in the practice of this invention and which are preferably solid include polyazelaic polyanhydride and polyadipic polyanhydride. These materials provide stability when and mixed with epoxy resin and become active fluxing and curing agents only when heated to their melting points.

Other crosslinking agents with fluxing properties which can be used are mono, di-and polyhydrazides which are solid at ambient temperature and insoluble in the monomer or polymer until heated, in practice generally to soldering temperature. A preferred such compound is adipic dihydrazide. Because of the differing reactivities of polycarboxylic acids and hydrazides, it is preferred to use a mixture of crosslinking agents, such as dodecanedioic acid and adipic dihydrazide, the higher reactivity of the latter being countered by the lower reactivity of the former.

While the oxide removed from the solder or a salt produced by reaction between the polyacid and such oxide, as a result of the fluxing activity of the crosslinking agent, acts as a catalyst for the curing of the polymer, curing in the manner of a snap cure fix is achieved only when a catalyst is present, such

catalyst being active at the elevated temperature utilised for soldering. A preferred such latent catalyst is an imidazole catalyst especially phenyl imidazole. This effect is often not desirable as it is contrary to the need to adjust positioning of components during soldering. Other latent reaction catalysts which can be used are tertiary amines with the amine groups optionally substituting the reactive monomer or polymer, as in the aforesaid Araldite MY10510 or MY9512, or metallic salts such as tin octanoate, dibutyl tin dilaurate, ferric acetylacetonate, and cobalt (III) acetylacetonate.

Preferred compositions embodying the invention will have a thermosetting polymer-crosslinking agent/flux content in which there are from 45 to 70%, more preferably 50 to 60%, by weight of thermosetting polymer and from 55 to 30% by weight, more preferably 50 to 40%, by weight crosslinking agent/flux.

These curing agents may be combined so as to produce a range of products which provide underfill rigidity ranging from

The use in adhesive compositions employed for encapsulating flip chip connections of ceramic powders to enhance thermal expansion and modulus properties of the composition has already been mentioned herein and is preferably to be adopted in the practice of the present invention. It is preferred that such ceramic powders be highly thermally conductive to enhance the connection between solder bump and conductor on the substrate while ensuring that the compositions retain the low viscosity necessary for fluxing and for ease of deposition. The filler is preferably a nominally 5μ diameter spherical ceramic bead or hollow sphere composition. More generally, it maybe a glass or ceramic powder comprising spherical particles of 0.1-25μ, preferably 1-15μ, diameter or comprise essentially

monodisperse spherical particles having a single diameter of 0.1-25μ, preferably 1-15μ. The ceramic powder has preferably a very high thermal conductivity. Examples of such ceramic powders which may be employed are SiO_2, MgO, Al_2O_3, TiO_2/ZnO, barium sulphate and diamond dust. In some cases, it is preferred that the ceramic powder utilised has instead a very low or negative coefficient of thermal expansion, too, and if this requirement is imposed on the ceramic powder then a preferred example is aluminium lithium silicate.

Metal oxides formed on solder metals even at ambient temperatures are themselves a problem since they can catalyse crosslinking of the thermosetting resin or its monomer precursor. In accordance with a preferred embodiment of the invention, the resin or precursor contains an acid flux which is liquid at temperatures below 100°C, preferably below 40°C, more preferably ambient temperature. This acid will react with oxides to form salts which will not decompose until at elevated temperatures, in particular soldering temperatures when the resulting oxides, together with oxides formed on the metal surfaces more readily at the higher temperatures and removed from the metal surfaces by the flux/crosslinking agent, will catalyse the crosslinking of the thermosetting polymer.

The term "acid" as such is used herein to denote the more volatile flux for preventing prepolymerisation/crosslinking and to distinguish it from the solid crosslinking agent/flux. The more volatile flux is generally liquid at ambient temperature so that it acts immediately as a flux. It should certainly be liquid, at least at temperatures below those at which the crosslinking agents used become fully reactive in the presence of metal oxide/salt crosslinking catalysts. It is thus preferred that the acid used for preventing

prepolymerisation, even if solid at ambient temperature, is liquid by 40°C.

Such liquid acids may be polyacids, but will normally be monocarboxylic acids. The acids preferably contain at least 8 carbon atoms and are exemplified by versatic acids, in particular versatic 10 which is a synthetic acid composed of a mixture of highly branched isomers of C_{10} monocarboxylic acids, mainly of tertiary structure. The high degree of branching gives rise to steric hindrance which means that the salts formed are thoroughly stable and difficult to break down. Other acids which may be used are capric acid, caprylic lauric acid, stearic acid and palmitic acid.

When such monocarboxylic acids are to be used, compositions embodying the invention preferably will have a thermosetting polymer - flux content in which there are 30 to 70%, more preferably 50 to 60%, by weight of thermosetting polymer and from 70 to 30%, more preferably 50 to 40%, by weight of a mixture of fluxes, the flux components consisting of from 80 to 97%, preferably 85 to 95%, by weight of solid crosslinking agent/flux and from 20 to 3%, preferably 15 to 5%, by weight of acid flux which is liquid at below 100°C.

When utilising the compositions of the invention, there is no need for them to be introduced subsequent to formation of a solder connection with the attendant difficulties identified above. It is possible for the composition to be predeposited, before emplacement and soldering of electronic component to substrate, on either or both of the electronic component and the substrate. As there is no need for a separate fluxing agent to be employed which is not incorporated in the adhesive composition, the presence of the composition on one or other of the electronic component and the substrate fulfils the required fluxing function.

Insofar as the composition may be applied to the electronic component, then this may be to the die overall whether it is in wafer form or as separate discrete devices. Application of the composition may be by screen printing, stencil printing, dispensing, spinning or any other known method for applying a composition to discrete areas.

The ease of working in accordance with the method of this invention enables the composition to contain the thermosetting resin in the form of a B-stageable precursor for application to die, substrate or carrier tape and then B-staging so as to form a handleable film which becomes fully crosslinked only when the soldering operation is carried out.

The following examples illustrate the adhesive compositions which may be used in the practice of this invention. In the examples all percentages are percentages by weight.

Example 1

ERL 4221	40.6%
MY9512	12.7%
DDDA	46.7%

This composition was functionally good and of satisfactory viscosity for most applications.

Example 2

ERL 4221	39.65%
Epoxy MY9512	12.40%
DDDA	41.05%
Versatic 10	6.90%

This composition was functionally good in not undergoing pre-crosslinking but had too low a viscosity for some applications. As a result, higher viscosity compositions as follows were made up and found to work well.

Example 3

ERL 4221	33.45%
MY9512	18.60%
DDDA	41.05%
Versatic 10	6.90%

Example 4

ERL 4221	26.05%
MY9512	26.00%
DDDA	41.05%
Versatic 10	6.90%

Example 5

ERL 4221	12.40%
MY9512	39.65%
DDDA	41.05%
Versatic 10	6.90%

The initial viscosity of the composition is here somewhat too high for ease of use. Moreover, while Examples 2 to 5 made use of monocarboxylic acids liquid at ambient temperature, it is also possible to use monocarboxlyic acids solid at ambient temperature but liquid at temperatures below those at which the crosslinking agent/flux are, for example, as follows:-

Example 6

ERL 4221	39.65%	
Epoxy MY9512	12.40%	
DDDA	41.05%	
Prifrac2960	6.90%	(C16 Palmitic acid - solid metals at 60°C)

Example 7

ERL 4221	39.65%
Epoxy MY9512	12.40%
DDDA	41.05%

Versatic 10 6.90% (C18 - melts at 69°C)

Finally compositions were formulated which contained lower amounts of monocarboxylic acid. These, too, proved to be satisfactory.

Example 8

ERL 4221	39.65%
MY9512	12.40%
DDDA	44.95%
Versatic 10	3.00%

Example 9

ERL 4221	42.62%
MY9512	13.33%
DDDA	41.05%
Versatic 10	3.00%

CLAIMS

1. A thermally curable adhesive composition which comprises:

(a) a thermosetting polymer, or a monomer which is polymerisable to yield a thermosetting polymer, said polymer being crosslinkable when subject to the action of a chemical crosslinking agent;

(b) a chemical crosslinking agent for said polymer, the crosslinking agent having fluxing properties and exhibiting no reactivity, or exhibiting very restricted reactivity with the polymer without the action of a catalyst and/or heat; and

which composition is thermally curable when heated to soldering temperatures in the presence of a catalyst for the crosslinking of the polymer with a crosslinking agent and is storage and reaction stable in the absence of such catalyst and at ambient temperatures.

2. A composition according to claim 1, wherein the chemical crosslinking agent is solid at ambient temperature.

3. A composition according to claim 1 or 2, wherein said chemical crosslinking agent is selected from polyacids, polyanhydrides and hydrazides which are solid at ambient temperature and insoluble in the monomer or polymer until heated to soldering temperature.

4. A composition according to claim 3, wherein the polyacid is selected from polymers containing two or more carboxyl groups and di- and polycarboxylic acids and di-and polyanhydrides.

5. A composition according to claim 4, wherein the

polycarboxylic acid is a C_8 or greater dicarboxylic acid.

6. A composition according to claim 3, wherein the hydrazide is a monohydrazide, dihydrazide or polyfunctional hydrazide.

7. A composition according to any one of claims 3 to 6, wherein the crosslinking agent contains a dihydrazide and/or a dicarboxylic acid.

8. A composition according to claim 7, wherein the crosslinking agent contains adipic dihydrazide and/or dodecanedioic acid.

9. A composition according to claim 4, wherein the crosslinking agent is a styrene acrylic acid copolymer.

10. A composition as claimed in any preceding claim which contains from 30 to 70 parts by weight of thermosetting resin.

11. A composition according to any one of claims 1-9, wherein said polymer is an epoxy resin.

12. A composition according to claim 11, wherein said polymer is a B-staged epoxy resin.

13. A composition according to claim 12, wherein the said polymer is a diglycidyl ether of bisphenol A.

14. A composition according to claim 10, wherein the said resin is a tri- or tetrafunctional epoxide or a difunctional cycloaliphatic epoxide or a mixture of two or more such epoxides.

15. A composition according to any preceding claim, which has a thermosetting polymer - solid crosslinking agent/flux content in which there are from 30 to 70% by weight of thermosetting polymer and from 70 to 30% by weight of solid crosslinking agent/flux.

16. A composition according to Claim 15, wherein said thermosetting polymer content is from 50 to 60% by weight and said solid crosslinking agent/flux content is from 50 to 40% by weight of the total amount of thermosetting polymer and crosslinking agent/flux.

17. A composition according to any preceding claim, which additionally contains an acid flux which is liquid at temperatures below 100°C.

18. A composition according to Claim 17, wherein the acid flux is liquid at ambient temperature.

19. A composition according to Claim 17 or 18, wherein the acid flux is a monocarboxylic acid, preferably containing at least 8 carbon atoms.

20. A composition according to Claim 19, wherein the acid flux is a versatic acid, capric acid, caprylic acid, lauric acid, stearic acid or palmitic acid.

21. A composition according to any one of Claims 17 to 20, which has a thermosetting polymer-flux content in which there are from 30 to 70% by weight of thermosetting polymer and from 70 to 30% by weight of flux, which flux is, in turn, made up from 80 to 97% by weight of said solid crosslinking agent/acid flux and from 20 to 3% by weight of said acid flux.

22. A composition according to Claim 21, which has a

thermosetting polymer-flux content in which there are from 50 to 60% by weight of thermosetting polymer and from 50 to 40% by weight of flux, which flux is, in turn, made up from 85 to 95% by weight of said solid crosslinking agent/flux and from 15 to 5% by weight of said acid flux.

23. A composition according to any preceding claim, which additionally contains a latent reaction catalyst selected from tertiary amines and imidazoles and metallic salts.

24. A composition according to Claim 23, wherein the imidazole is phenyl imidazole.

25. A composition according to Claim 23, wherein the tertiary amine is constituted by self catalysing tertiary amine groups substituting the reactive monomer or polymer.

26. A composition according to Claim 25, wherein the reactive monomer is a tertiary amine-substituted trifunctional or tetrafunctional epoxide.

27. A composition according to Claim 23, wherein the metallic salt is tin octanoate, dibutyl tin dilaurate, ferric acetylacetonate, and cobalt (III) acetylacetonate.

28. A composition according to any preceding claim which further comprises a thermally conductive filler.

29. A composition according to Claim 28, wherein said filler reduces thermal expansion of the composition while not effecting substantially the viscosity thereof.

30. A composition according to Claims 28 and 29, wherein the filler is constituted by nominally 5μ spherical ceramic beads or hollow spheres.

31. A composition according to Claim 28, wherein the filler is a ceramic or glass ceramic powder comprising spherical particles with diameters in the range from 0.1 to 25μ, preferably 1-15μ.

32. A composition according to Claim 28, wherein the filler is a ceramic or glass ceramic powder consisting essentially of monodisperse spherical particles having a single diameter in the range from, 0.1 to 25μ, preferably 1-15μ.

33. A composition according to Claim 28, wherein the filler is a thermally conductive ceramic powder.

34. A composition according to Claim 33, wherein the ceramic powder is selected from SiO_2, MgO, Al_2O_3, TiO_2 /ZnO, barium sulphate and diamond dust.

35. A composition according to Claim 28, wherein the ceramic powder has a low or negative coefficient of thermal expansion.

36. A composition according to Claim 35, wherein the ceramic material is aluminium lithium silicate.

37. A method of producing an electronic device which comprises opposing an electrical component having a plurality of electrical terminations, each termination including a solder bump, and a component-carrying substrate having a plurality of electrical terminations corresponding to the terminations of the electrical component, with a thermally curable adhesive

composition according to any one of claims 1 to 36 being applied to a metal surface at one and/or both of said electrical component and said substrate, bringing the electrical component and substrate into contact at elevated temperature and thereby soldering the electrical component to the substrate and simultaneously achieving encapsulation thereof in thermoset polymer produced from said monomer or polymer in situ, catalysis of crosslinking of the thermally curable adhesive being achieved by metal oxide removed from metal surfaces by the fluxing composition and/or salts formed by reaction between metal oxide and crosslinking agent.

38. A method as claimed in Claim 37, wherein the thermally curable adhesive composition is applied to one and/or both of the said electrical component and said substrate prior to bringing the two together.

39. A method as claimed in Claim 37 or 38, wherein no fluxing agent is applied to either said electrical component or said substrate prior to application of the solder curable adhesive composition.

40. A method as claimed in any one of Claims 37 to 39, wherein the thermally curable adhesive composition is applied to a die, which is either in wafer form or as separate discrete devices.

41. A method as claimed in any one of Claims 37 to 40, wherein the thermally curable adhesive composition is applied by screen printing, stencil printing, dispensing or spinning.

42. A method as claimed in any one of Claims 37 to 41, wherein the thermally curable adhesive composition is

applied in B-stageable form and B-staged in situ.